

# Towards the conversion of carbohydrate biomass feedstocks to biofuels *via* hydroxymethylfurfural

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Received 8th December 2009, Accepted 3rd July 2010

DOI: 10.1039/b925869h

This review appraises the chemical conversion processes recently reported for the production of hydroxymethylfurfural (HMF), a key biorefining intermediate, from carbohydrate biomass feedstocks. Catalytic sites or groups required for the efficient and selective conversion of hexose substrates to HMF are examined. The principle of concerted catalysis was used to rationalise the dehydration of fructose and glucose to HMF in non-aqueous media. A survey of reported reaction routes to diesel-range biofuel intermediates from HMF or furfural is presented and self-condensation reaction routes for linking two or more HMF and furfural units together toward obtaining kerosene and diesel-range biofuel intermediates are highlighted. The reaction routes include: benzoin condensation, condensation of furfuryl alcohols, hetero Diels–Alder reaction and ketonisation reaction. These reaction routes are yet to be exploited despite their potential for obtaining kerosene and diesel-range biofuel intermediates exclusively from furfural or hydroxymethylfurfural.

## 1. Introduction

Our global society is rapidly evolving and the demand for energy is increasing at a high rate. More than eighty percent of worldwide energy needs are presently being met from fossil fuels and other non-renewable energy resources. In particular, the transportation sector, which is witnessing the fastest growth rate in energy consumption, derives its fuels almost entirely from petroleum crude. Correspondingly, this sector also has associated with it the highest growth rate in the emission of green house gases (GHGs) over the last decade. However, increasing anthropogenic emission of GHGs had been linked to global warming; and global warming is a major concern worldwide. This accounts for the global advocacy for a paradigm shift from

fossil fuels energy resources to renewable energy systems. Another motivation for the search for alternatives to fossil fuels is the quest for some measure of independence and security in terms of energy supply. Extensively investigations are being carried on development of efficient and economic systems for harnessing energy from carbon-free renewable sources (such as solar, hydroelectric, wind, geothermal, tidal and nuclear) in order to expand the spectrum of their applications at competitive prices compared to the existing fossil fuels based systems.<sup>1,2</sup>

However, the application of carbon-free renewable energy resources in the transportation sector appears not to be feasible in the near future. Hence, the production of transportation fuels from carbon-neutral biomass is widely accepted as a sustainable alternative to petroleum-derived fuels. In this respect, the biofuel market has increased greatly in recent times and a competitive biofuels sector has become or assumed both national and global strategic goals towards sustainable development. In this sector, bioethanol and biodiesel (from carbohydrate and lipid biomass respectively) are the main global biofuel commodities. Although bioethanol and biodiesel are classified as first generation biofuels,

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### Broader context

Short-carbon-chain alcohols (ethanol and butanol) are the most prominent biofuels from carbohydrate biomass. Production of these biofuels is based on relatively slow fermentation and energy-demanding distillation processes. In recent times, the range of biofuels obtainable from carbohydrate biomass has increased considerably with the use of faster and energy efficient chemical catalytic methods. One of the products of chemical catalytic methods is dimethylfuran (DMF). DMF is considered to be a better fuel than ethanol in terms of production efficiency, energy density, handling and storage. This has led to greater interest in chemical catalytic methods for producing a wide range of fuels from carbohydrate substrates. To this end, hydroxymethylfurfural (HMF) has been identified as a key intermediate. To date kerosene and diesel-range fuel intermediates have not been produced from HMF without the need for complementary compounds or feedstocks (obtained using a biological method or derived from petroleum). Here, we point out that kerosene and diesel-fuel intermediates can be obtained with HMF alone as the feedstock *via* self-coupling (C–C bond formation). The resulting intermediates can then be converted to their respective fuels in a single step *via* hydrogenolysis as in the case of HMF to DMF.

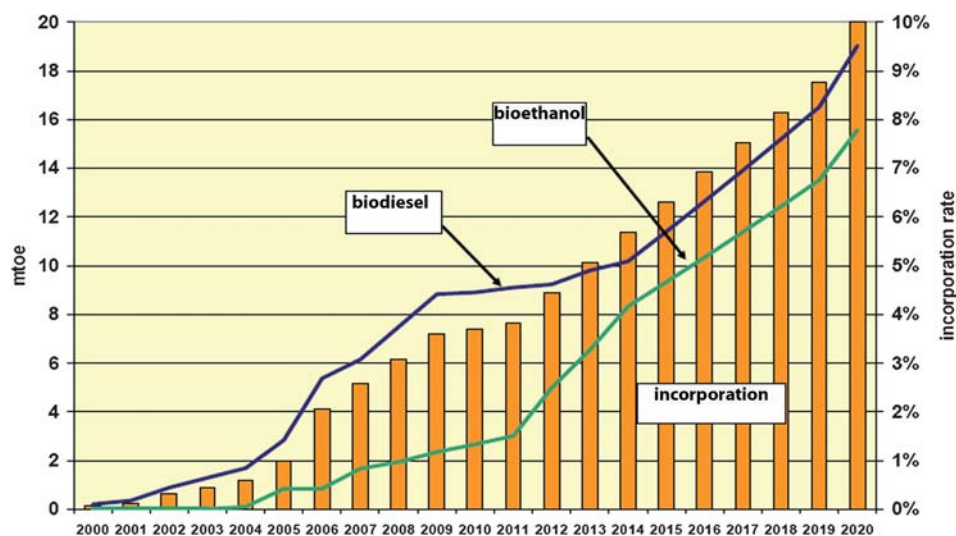


Fig. 1 Biodiesel and bioethanol demand and the incorporation rate until 2020 in the .

their production has been associated with concerns about adverse effect on global food supply, loss of forest resources and threats to biodiversity; the rate of consumption of biodiesel and its incorporation rate in the energy mixed target of the European

Commission for the transportation sector significantly outpaced that of bioethanol (see Fig. 1).<sup>2,3</sup>

This is due to the properties of biodiesel which make it a closer substitute for its petroleum counterpart than bioethanol.



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Tropsch synthesis, biomass chemicals.

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Sudip Maity

non-thermal plasma techniques. He has several patents and publications.

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Biodiesel can be used directly in diesel engines without prior modification. Conversely, bioethanol is not a close substitute for petrol and it cannot be used directly in petrol engines. It is generally employed as a blend with petrol up to 85%, E85, in flexible fuel vehicles. In addition, ethanol is highly hygroscopic and slightly corrosive. Biodiesel is typically produced through chemical catalytic methods and the net energy balance of the process is generally adjudged to be significantly positive. Most commercial processes for conversion of carbohydrate biomass to biofuels are *via* biological methods which are characterised by slower reaction rates than chemical catalytic methods. Also, the net energy balance of bioethanol production *via* fermentation of sugars followed by distillation had been indicated to be low and in some cases negative.<sup>4</sup>

Carbohydrate biomass resources are abundant, widely distributed and cheaper than lipid biomass, thus, production of biofuels from carbohydrate biomass is expected to be more sustainable than lipid biomass. The above, in addition to the aforementioned limitations of bioethanol as a direct substitute for petrol, has inspired the development of chemical catalytic methods for producing promising biofuels from carbohydrate biomass. In this regard, hydroxymethylfurfural (HMF) had been identified as a key biorefining intermediate for chemicals and biofuels. The potential of HMF as a biofuel intermediate had been demonstrated by Dumesic and associates.<sup>5,6</sup>

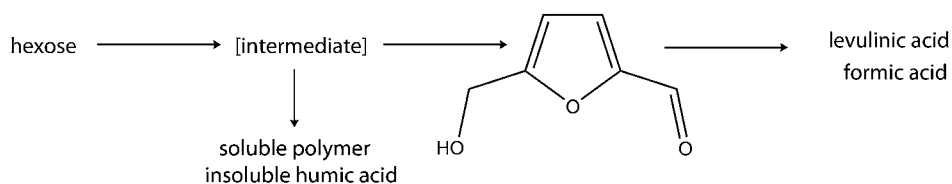
A biofuel that will qualify as a transportation fuel needs to meet criteria that are similar to their counterparts obtained from petroleum. The molecular formula of HMF,  $C_6H_6O_3$ , reveals that it is oxygen rich and hydrogen deficient compared to other petroleum-derived fuels. Its conversion to a compound that will be useful as a transportation fuel requires processes that will deplete and enrich its oxygen and hydrogen contents respectively. It is also obvious from the molecular formula that HMF is not of sufficiently long carbon chain to produce a compound that will be suitable as a diesel-range fuel. One of the strategies used for increasing the carbon chain length of HMF involves carbon-carbon (C-C) coupling through condensation with a suitable compound of appropriate carbon length. This yields another intermediate compound which can be subsequently transformed to diesel-range biofuel by decreasing its oxygen and increasing its hydrogen content. It is observed that the need to couple HMF (through C-C bond formation) with another compound (which implies another feedstock) in order to form a diesel-range intermediate from HMF was due to the limitation imposed by the reaction route adopted. HMF is a multifunctional molecule that can undergo a variety of reactions including self-condensation through C-C bond formation which can afford intermediates to kerosene and diesel-range fuels. These self-condensation reactions of HMF are yet to be explored toward biofuel production. The highlights of these reactions constitutes the

main focus of the paper. However, for a better appreciation of the conversion processes from carbohydrate substrates to biofuels, we appraise recent developments in the production of HMF from different substrates.

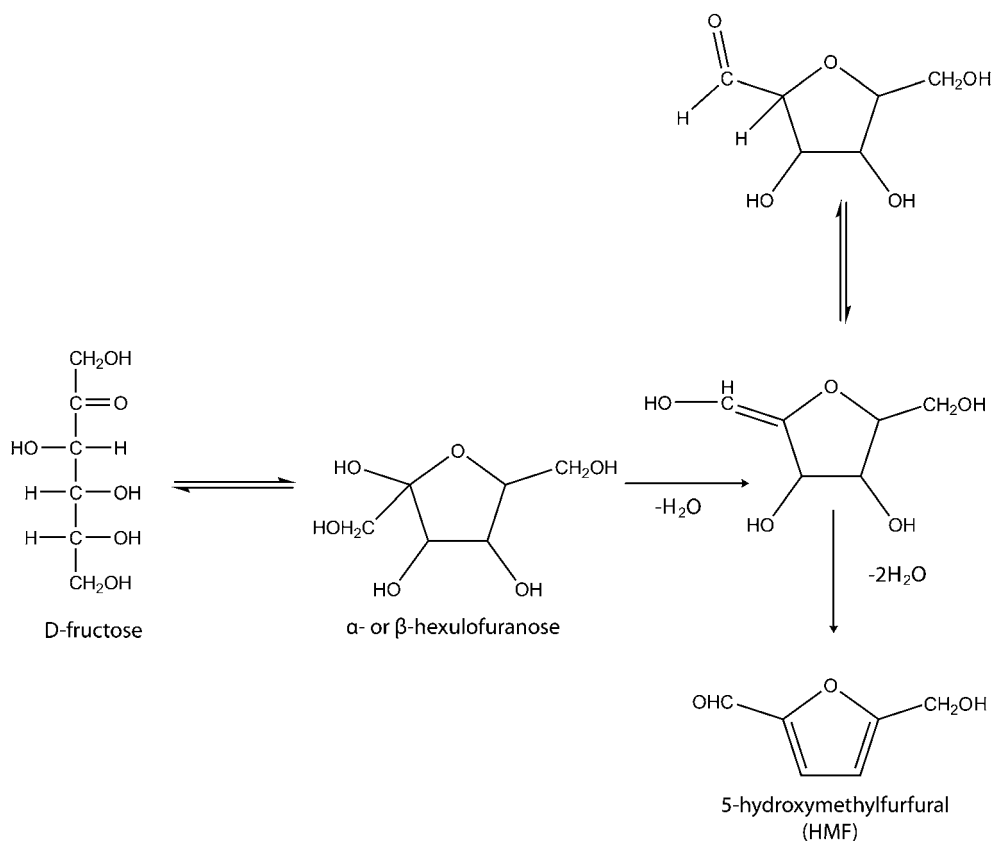
## 2. Production of hydroxymethylfurfural

HMF is expected to play a central role as a precursor to chemicals and biofuels from carbohydrate biomass. Hence a cheap, readily available starting material and efficient process for the commercial production of HMF is one of the major challenges that needs to be solved in order to make biofuels competitive with fossil fuels. Although the investigation of the chemistry of HMF dates back to the 19th century, research on this important chemical is still ongoing. Past research findings in this area are summarised in review reports, notable among which are those of Faury *et al.*,<sup>7</sup> Kustar,<sup>8</sup> Cottieras and Desertes<sup>9</sup> and lately Lewkowsky.<sup>10</sup> The report of Lewkowsky on this subject to the best of our knowledge appears to be the most recent and exhaustive. It discusses the synthesis, chemistry and applications of HMF and its derivatives. It also highlights the important aspects of previous reviews by several researchers.

It is generally accepted that the synthesis of HMF is based on the triple dehydration of hexose (Scheme 1). Apart from hexoses, other substrates that can be used are oligo- and polysaccharides. The dehydration reaction can occur in either aqueous or non-aqueous media, usually in the presence of acid catalysts. The dehydration of hexoses to HMF, when carried out in non-aqueous media, is found to be more efficient in terms of HMF yield and reaction temperature than those in aqueous media. The higher HMF yields in non-aqueous solvents have been attributed wholly or in part to the inhibition of the degradation of HMF to levulinic acids. Non-aqueous solvents such as dimethylsulfoxide (DMSO), *n*-butanol, acetone, dioxane, polyglycol ether and dimethylformamide (DMF) have been used as the reaction medium in the dehydration of hexose to HMF. Among the non-aqueous solvents, reports on the use of DMSO constitute the greatest number in the literature. The dehydration of fructose in DMSO was also found to be possible in the absence of a catalyst.<sup>11</sup> However, the use of these solvents also suffers from the drawback of the poor solubility of hexose and the problem of separation of the HMF from the reaction medium. In addition, there are concerns about the economic feasibility and ecological impact of the use of the non-aqueous solvents in the large-scale production of HMF.<sup>12,13</sup> This may account for why there is not yet a process based on a non-aqueous medium system for the commercial production of HMF. However, the solubility problems can be addressed by the application of mixed-solvent (water-organic) systems. Here non-aqueous solvents are usually



Scheme 1 Dehydration of hexose to HMF.



**Scheme 2** Mechanism of fructose dehydration to HMF.<sup>5</sup>

miscible with water and thus act as phase modifiers of the aqueous medium.

The common hexose substrates normally used for the production of HMF are fructose and glucose. It has been established from studies that fructose is more reactive than glucose under identical conditions. Hence, fructose is a more efficient and selective substrate than glucose in the synthesis of HMF. Glucose and fructose can be in their cyclic and acyclic forms in aqueous and non-aqueous media; hence, their dehydration to HMF has been proposed to be possible through either cyclic or acyclic pathways. Moreover, it has been experimentally demonstrated by Antal *et al.*<sup>12</sup> that the mechanism of formation of HMF from hexose is *via* cyclic intermediates. It involves the sequential elimination of three molecules of water from the hexose substrate in its cyclic form (see Scheme 2). The elimination of the first water molecule is the rate-determining step. It leads to an enol intermediate and is hence tagged the ‘enolisation’ step. Fructose enolyses more readily than glucose, this accounts for why most studies on the synthesis of HMF involve the use of fructose as the substrate.

## 2.1 Catalytic site requirement for selective conversion of fructose to HMF

In this section, we attempt to identify and draw attention to the catalytic site requirements for the efficient and selective conversion of fructose to HMF. The dehydration of fructose is known to be catalysed by Brønsted acids as well as Lewis acids. The

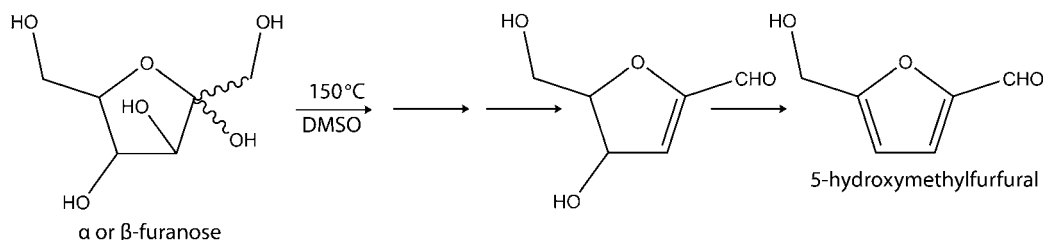
review by Lewkowski<sup>10</sup> indicates that nearly a hundred inorganic and organic compounds positively qualify as catalysts for the synthesis of HMF. The catalysts are divided into five groups (see Table 1).

Dehydration of fructose to HMF is traditionally carried out in aqueous media. The reaction is generally characterised by poor selectivity for HMF. However, a number of reports showed that selectivity for HMF is enhanced when the reaction is carried out in non-aqueous media, notably dimethylsulfoxide (DMSO) and ionic liquids.<sup>13</sup>

**2.1.1 Dehydration of fructose in DMSO.** It has also been reported that the dehydration of fructose can take place in DMSO in the absence of any catalyst.<sup>14</sup> This poses a question about the nature of the catalytic site(s) or group(s) which is/are required for the selective and efficient dehydration of hexose substrates to HMF. A recent NMR study on the mechanism of the dehydration of fructose to HMF appears to give some clues as to the question raised above.<sup>14</sup> It was shown that the anomeric composition of D-fructose in DMSO changes when the mixture is heated from room temperature to 150 °C, there is small increase in the  $\alpha$ -fructose formation at the expense of the  $\beta$ -pyranose tautomer. A small amount of the  $\alpha$ -pyranose form was also observed at 150 °C. The mechanism proposed to explain the dehydration of the two forms of D-fructose to HMF *via* the elimination of three molecules of water is presented in Scheme 3. The mechanism is based on the direct identification of an intermediate involved in the reaction. A critical analysis of the

**Table 1** Groups of catalysts used in the synthesis of HMF<sup>10</sup>

Organic acids	Inorganic acids	Salts	Lewis acids	Others
oxalic acid levulinic acid maleic acid <i>p</i> -TsOH	phosphonic acids sulfuric acid hydrochloric acid iodine or hydroiodic acid generated <i>in situ</i>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> /SO <sub>3</sub> pyrid/PO <sub>4</sub> <sup>3-</sup> aluminium salts Th and Zr ions/zirconium phosphates Ions: Cr, Al, Ti, Ca, In ZrOCl <sub>2</sub> VO(SO <sub>4</sub> ) <sub>2</sub> , TiO <sub>2</sub> Zr-, Cr-, Ti-porphyrin	ZnCl <sub>2</sub> AlCl <sub>3</sub> BF <sub>3</sub>	ion-exchange resins zeolites

**Scheme 3** Dehydration of fructose to HMF in DMSO.

mechanism could lead to an insight into the design of catalysts with a high performance for HMF production.<sup>14</sup>

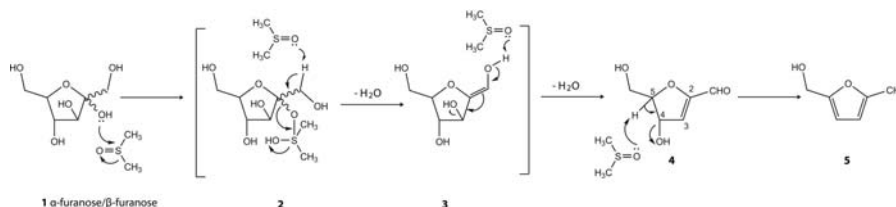
According to Hegarty and Dowling,<sup>15</sup> enolisation of aldehydes in aqueous media is *via* concerted catalysis. These authors report that at high buffer concentrations the enolisation of aldehydes is markedly catalysed simultaneously by acidic and basic species. It was also asserted that concerted catalysis is largely independent of the buffering species, and that the process is overall base catalyzed.<sup>16</sup> A similar phenomenon was reported to account for the efficiency and selectivity of the enzyme catalysed isomerisation of glucose to fructose. The catalytic activity of the enzyme was attributed to the synergistic activation of the substrate (glucose) by a Lewis acid and a weak Brønsted acid sites.<sup>17</sup> The acid–base bi-functional model in aqueous media can be correlated with electrophilic and nucleophilic concept in non-aqueous media.

DMSO is a polar compound with a dipole on the S–O bond. The sulfur end of the bond is electrophilic while the oxygen end is nucleophilic. The observed increase of  $\alpha$ -furanose at the expense of  $\beta$ -pyranose can be attributed to the isomerisation of  $\beta$ -pyranose to  $\alpha$ -fructose (glucose to fructose) *via* synergistic activation by the nucleophilic and electrophilic parts or ends of the DMSO. As illustrated in the mechanism proposed by Ananda and associates<sup>14</sup> (Scheme 4), the initiation step in dehydration of fructose to HMF in DMSO is *via* simultaneous activation of the OH

group on the C<sub>2</sub> of fructose by the electrophilic end of DMSO and H-bonding interaction between the nucleophilic end of DMSO and one of the hydrogen atoms on C<sub>1</sub> of the fructose. Elimination of the first molecule of water is accomplished as a result of the ease of proton transfer and oxygen exchange with DMSO.

The OH group at the anomeric centre of fructose attacks the electrophilic (sulfur) centre of DMSO. This brings about the formation of a covalent bond between the sulfur atom of DMSO and the oxygen atom at the anomeric centre of the substrate. This is also accompanied by a proton transfer from the OH of the anomeric centre of fructose to oxygen atom in DMSO. The H-bonding interaction between one of the hydrogen atoms on C<sub>1</sub> and a nucleophilic centre of another DMSO molecule facilitates its elimination and the simultaneous cleavage of the C–O bond of the anomeric centre and the S–OH bond of DMSO in the DMSO–substrate complex/intermediate. An enol intermediate is formed through the exchange of an oxygen atom between DMSO and the OH oxygen atom at the anomeric centre of fructose and removal of the hydrogen atom from C<sub>1</sub> and an OH group from the S–OH as water. The removal of the remaining two molecules of water is promoted by the nucleophilic centre (oxygen) of DMSO.

It can be said that the concerted catalysis at the initiation or enolisation step reduces the chances of condensation or

**Scheme 4** Mechanism for the dehydration of the furanose D-fructose forms **1** ( $\alpha$ -furanose/ $\beta$ -furanose) to 5-hydroxymethylfurfural (**5**) in DMSO at 150 °C.<sup>14</sup>



**Table 2** Some reported results of dehydration of fructose in ionic liquids<sup>a, b, c</sup>

	Ionic liquid	Reaction <i>T</i> /°C	Reaction time	HMF yield (%)	Ref.
1	BMIM <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	80	3 h	40–50	18
2	BMIM <sup>+</sup> BF <sub>4</sub> <sup>-</sup> (with concurrent HMF extraction with toluene)	80	3 h	85	18
3	HMIM <sup>+</sup> Cl <sup>-</sup>	90	15–45 min	92	19
4	EMIM <sup>+</sup> Cl <sup>-</sup>	80–120		63	20
5	EMIM <sup>+</sup> Cl <sup>-</sup> (with transition metal chloride)	80–120		85	20

<sup>a</sup> HMIM<sup>+</sup>Cl<sup>-</sup>: 3-methylimidazolium chloride. <sup>b</sup> EMIM<sup>+</sup>Cl<sup>-</sup>: 1-ethyl-3-methylimidazolium chloride. <sup>c</sup> BMIM<sup>+</sup>BF<sub>4</sub><sup>-</sup>: 1-butyl-3-methylimidazolium tetrafluoroborate.

polymerisation side reactions. Also, the absence of aqueous protons in the system prevents subsequent degradation of the HMF to levulinic acid. This demonstrates that bifunctional catalytic systems with readily accessible nucleophilic and electrophilic sites are required for the selective and efficient conversion of fructose to HMF.

**2.1.2 Dehydration of fructose in ionic liquids.** A number of papers on the selective dehydration of fructose and its polymer in ionic liquids, with or without acid catalysts, have appeared in the literature.<sup>18–27</sup> Dehydration of fructose to HMF was reported at much lower temperatures than in aqueous and mixed aqueous organic systems. The mechanism of dehydration of fructose to HMF in ionic liquids can also be accounted for by concerted catalysis. In these cases, the cation and the anion of an ionic liquid act as electrophile and nucleophile respectively. They simultaneously activate the substrate to promote the enolisation step. Subsequent elimination of water is driven by the anions (which are more accessible) of the ionic liquid. This explanation can be extended or extrapolated to account for the observed sequence of developments on the use of ionic liquid systems for the dehydration of fructose to HMF.

Despite active investigations on the use of ionic liquids in the dehydration of fructose to HMF, the main focus of most of reports on the subject has been the development of efficient (low temperature) and selectivity (high yield of HMF) systems. There is a literature gap on the mechanism of dehydration of fructose to HMF in ionic liquid systems, as reported for DMSO systems. However, a critical analysis of the results presented in Table 2 reveals that the nature of the reaction medium used in the dehydration of fructose to HMF in ionic liquids is similar to that in DMSO. This suggests that the same mechanism may account for the catalytic actions in the two systems. It implies that the catalytic action of ionic liquids can also be explained in terms of concerted catalysis, as described earlier in DMSO. The catalytic action of ionic liquids can thus be rationalised in a similar manner as follows: The conversion of fructose to HMF is *via* a sequence of consecutive elementary steps, leading to the elimination of three molecules of water. The rate-determining step is the enolisation of fructose by the concerted activation of fructose at the C–OH bond of the anomeric carbon by the cation (electrophile) of the ionic liquid and at the C–H of C<sub>1</sub> of the fructose *via* hydrogen bonding by an anion (nucleophile) of the ionic liquid. This will result in the elimination of the first molecule of H<sub>2</sub>O and formation of the enol intermediate. Again,

subsequent elimination of the second and the third molecules of water is facilitated by hydrogen-bonding interaction of the anions of the ionic liquid with the hydrogen of the OH groups at C<sub>1</sub> and the hydrogen at C<sub>5</sub> of the intermediate respectively. Thus, it can be said that the catalytic action of the ionic liquid in the dehydration reaction will be enhanced by accessibility of the cation and the hydrogen-bonding strength of the anion.

Therefore, the observed catalytic performance (low temperature of 90 °C and the high yield of 92%) of HMIM<sup>+</sup>Cl<sup>-</sup> can be attributed to concerted catalysis by the HMIM<sup>+</sup> cation and Cl<sup>-</sup> anion and not due to HMIM<sup>+</sup>Cl<sup>-</sup> acting as a proton reservoir as suggested by Moreau and co-workers.<sup>19</sup> The lower performance of EMIM<sup>+</sup>Cl<sup>-</sup> compared to HMIM<sup>+</sup>Cl<sup>-</sup> can be linked to the reduced accessibility of the cation in facilitating the enolisation step. The observed enhancement of the catalytic action of EMIM<sup>+</sup>Cl<sup>-</sup> on addition of metal halides can be attributed to the ability of the metal cations to substitute for the cation of the ionic liquid as a soft Lewis acid and/or readily accessible electrophile for the concerted catalysis step.

In a report by Qi and co-workers,<sup>22</sup> 1-butyl-3-methylimidazolium chloride, BMIM<sup>+</sup>Cl<sup>-</sup>, efficiently dehydrates fructose to HMF with a sulfonic ion-exchange resin as the catalyst. A fructose conversion of 98.6% and a HMF yield of 83.3% were reported after 10 min of reaction at 80 °C. The reaction time was reduced to 1 min when the temperature was increased to 120 °C which resulted in an HMF yield of 82.2% and nearly 100% fructose conversion. Comparison of the BMIM<sup>+</sup>Cl<sup>-</sup> and BMIM<sup>+</sup>BF<sub>4</sub><sup>-</sup> systems, each with a sulfonic ion-exchange resin as the catalyst, indicates that the higher efficiency and selectivity observed in the BMIM<sup>+</sup>Cl<sup>-</sup> system can be attributed to a higher tendency towards concerted catalysis due to the greater hydrogen-bonding character, nucleophilicity or basicity of the chloride ion. Also, when the dehydration reaction in the BMIM<sup>+</sup>Cl<sup>-</sup>/sulfonic acid system is compared with that of EMIM<sup>+</sup>Cl<sup>-</sup> and EMIM<sup>+</sup>Cl<sup>-</sup>/CrCl<sub>2</sub>, it would have been expected that the less bulky EMIM<sup>+</sup> should give a higher HMF yield compared to BMIM<sup>+</sup>. In contrast, the BMIM<sup>+</sup>Cl<sup>-</sup>/sulfonic acid system was reported to exhibit a higher efficiency than the EMIM<sup>+</sup>Cl<sup>-</sup> system. The result can be rationalised as arising from the presence of a sulfonic ion-exchange resin in BMIM<sup>+</sup>Cl<sup>-</sup> which generates protons in the system. The proton is a more readily accessible electrophile than EMIM<sup>+</sup>. In the above case, the anions are identical (Cl<sup>-</sup>) but the cations are different. The observed catalytic performance illustrates the importance of the accessibility of the electrophile as suggested earlier.

Moreover, a comparison of the EMIM<sup>+</sup>Cl<sup>-</sup>/CrCl<sub>2</sub> system with the BMIM<sup>+</sup>Cl<sup>-</sup>/sulfonic ion-exchange resin shows that the two systems produce similar yields of HMF (83.0% and 83.3% respectively). Based on the fact that the addition of CrCl<sub>2</sub> to EMIM<sup>+</sup>Cl<sup>-</sup> affords the dehydration of fructose to HMF at lower temperatures than in EMIM<sup>+</sup>Cl<sup>-</sup> alone, it can be suggested that electrophilicity and/or nucleophilicity may have been enhanced or extra electrophilicity and/or nucleophilicity introduced into the system. More fundamental studies are required to clarify the factors responsible for this observation. The accessibility of the electrophile is essential to the efficiency of the dehydration process. It is also important to note that the conversion of fructose was observed to be affected by the presence of water above a threshold of 5% in the BMIM<sup>+</sup>Cl<sup>-</sup>/H<sup>+</sup> resin system. This may be attributed to interference in the concerted catalysis as a result of the hydrogen-bonding interaction between the substrate (fructose) and water molecules. The report of Bao *et al.*<sup>21</sup> also lends support to this hypothesis in respect of the influence of the hydrogen-bonding character of the anion. The cations of the ionic liquids used are identical but the anions are different. Ionic liquids with higher hydrogen-bonding strengths have been reported to be more effective than those with lower hydrogen-bonding strengths.

A recent report indicates that an ionic liquid–tungsten salt catalyst system can dehydrate fructose to HMF at much lower temperatures (less than 50 °C) and at ambient pressure.<sup>23</sup> The hexahalides of tungsten, WCl<sub>6</sub>, was used as the catalyst. The unprecedented efficiency of this system calls for a critical analysis. Perhaps it could lead to more insight into the pathway of an economical process for the production of HMF. WCl<sub>6</sub> is known to have a zero dipole moment, one of the rare examples of a charge-neutral hexachloride. It has octahedral geometry with equivalent W–Cl bond length (2.24–2.26 Å), which accounts for the zero value of its dipole moments. Although a chloride ion and a covalently bonded chlorine atom are nucleophilic, the chloride ion Cl<sup>-</sup> is basic, while a chlorine atom in a non-polar covalent bond is neutral. However, the basicity of a covalently bonded chlorine atom increases with increasing dipole moment of the bond. This could suggest that covalently bonded chlorine atoms interact with the hydrogens in the intermediate in such a manner that it more efficiently promotes the elimination of water than the chloride ion. This may explain the observed lowering of the dehydration temperature by about 30 °C in the dehydration of mono- and polysaccharides using a biphasic reactor system.<sup>24</sup> The system comprised a reactive aqueous phase modified with DMSO and an organic extractive phase consisting of 7 : 3 (w/w) methyl isobutyl ketone (MIBK)/2-butanol mixture or dichloromethane (DCM). The reactions with the MIBK/2-butanol mixture were carried out at 443 K with mineral acids in a pH range of 1.0 to 2.0, while the reaction with DCM as the extracting solvent was conducted at 413 K and was reported not to require the use of an acid catalyst. The higher efficiency (in terms of decrease in dehydration temperature) reported with DCM as the extractive phase can be explained as being due to the presence of DCM in the reactive phase (even in catalytic amounts). Dehydration of fructose to HMF is known to occur in DMSO at reaction temperature in the absence of catalysts. DCM has two covalently bonded chlorine atoms and has a very low dipole moment; hence the covalently bonded chlorine atoms are

nucleophiles that promote the elimination of water molecules from fructose and the reaction intermediates. Hence, the combined catalytic effects of DMSO and DCM account for the decrease in the dehydration temperature, even in the absence of a catalyst. It may therefore be suggested that non-polar halogen compounds, such as CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>Cl, SiCl<sub>4</sub>, PCl<sub>5</sub> *etc.*, would have a tendency to exhibit similar catalytic effects as WCl<sub>6</sub> in the ionic liquid dehydration of fructose.

## 2.2 Production of HMF from glucose

The use of glucose as the substrate for the production of HMF faces the problem of the very low reactivity of glucose in most reaction systems in which fructose is readily converted to HMF. Despite this fact, the use of glucose is still desirable because of its lower price compared to fructose. For example, it was reported that glucose does not significantly react in HMIM<sup>+</sup>Cl<sup>-</sup>.<sup>19</sup> Only 3% glucose was converted after 30 min at a temperature of 90 °C. Under the same conditions, a 42% HMF yield was obtained with fructose. A dramatic change in the reactivity of glucose in EMIM<sup>+</sup>Cl<sup>-</sup> at 100 °C was reported with the addition of a catalytic amount of CrCl<sub>2</sub>. An HMF yield of 68–70% was obtained with CrCl<sub>2</sub>. Other metal halides investigated gave much lower HMF yields. The unprecedentedly high yield obtained with CrCl<sub>2</sub> was explained as being due to the formation of a complex, [EMIM]<sup>+</sup>[CrCl<sub>3</sub>]<sup>-</sup>, due to interaction of EMIM<sup>+</sup>Cl<sup>-</sup> and CrCl<sub>2</sub>. It was proposed that the CrCl<sub>3</sub><sup>-</sup> anion promotes proton transfer and hydride shift in the substrate. Proton transfer facilitates the mutarotation of glucose in EMIM<sup>+</sup>Cl<sup>-</sup>, while hydride shift leads to isomerisation of glucose to fructose. The fructose is then subsequently dehydrated to HMF *via* concerted catalysis in EMIM<sup>+</sup>Cl<sup>-</sup>. Since the conversion of glucose to HMF was indicated to proceed *via* a fructose intermediate, we briefly examine glucose–fructose isomerisation before we continue on the conversion of glucose to HMF

### 2.2.1 Glucose–fructose isomerisation in aqueous media.

Chemical isomerisation of glucose to fructose is traditionally carried out in aqueous solution at high pH and temperature. The reaction is characterised by low fructose selectivity due to the formation of by-products. In contrast, enzyme-catalysed glucose isomerisation is characterised by high fructose selectivity under mild reaction conditions (temperature 55–60 °C and pH 7.0–7.8).<sup>11</sup> The high fructose selectivity was attributed to the synergistic activation of glucose by Lewis acid and weak Brønsted acid sites on the enzyme. This is equivalent to the concerted catalysis being discussed in this review. The mechanism of the transformation is usually presented using the acyclic structure of the substrate (glucose). The Lewis acid site on the enzyme activates the carbonyl carbon to form an enolate intermediate. The Brønsted acid sites then donate a proton to the intermediate. The combined effect is a hydride shift, which transforms the intermediate to the enediol. Subsequent abstraction of the proton from the enediol intermediate by the conjugate base of the acid produces the ketose product (fructose).

In an alkali-catalysed system, the hydroxide ion tends to abstract a proton from the  $\alpha$ -carbon of the carbonyl carbon to generate a carbanion. The carbanion intermediate is a reactive species; it is prone to self- or cross-condensation reactions.

Moreover, the absence of a complementary catalytic site, *e.g.*, a Brønsted acid site, which synergistically drives the reaction path to the ketose product also accounts for the low selectivity of the alkali-catalysed glucose–fructose isomerisation. A modification of the aqueous reaction medium has been shown to affect the isomerisation reaction rate. Kinetic studies of alkaline isomerisation of glucose and fructose in 0.1 M ethanol solution showed that the isomerisation of glucose to fructose, and *vice versa*, was accelerated markedly as the alcohol concentration increased. The reaction rates in 70% ethanol solution were found to increase 2.4 and 1.7 times the corresponding values in water solutions.<sup>28</sup> The increased reaction rates could be attributed to the higher Brønsted acidity of ethanol compared to water which complements the hydroxide ion in promoting the isomerisation reaction. The reduced hydrogen-bonding strength of the reaction medium may also be a contributing factor. Reports on investigations on the use of solid bases as catalysts for glucose isomerisation have revealed that a number of solid bases displayed high selectivities for fructose but had low glucose conversion. The high fructose selectivities have links to the acid–base bifunctionality of the solid base catalyst.<sup>29–34</sup>

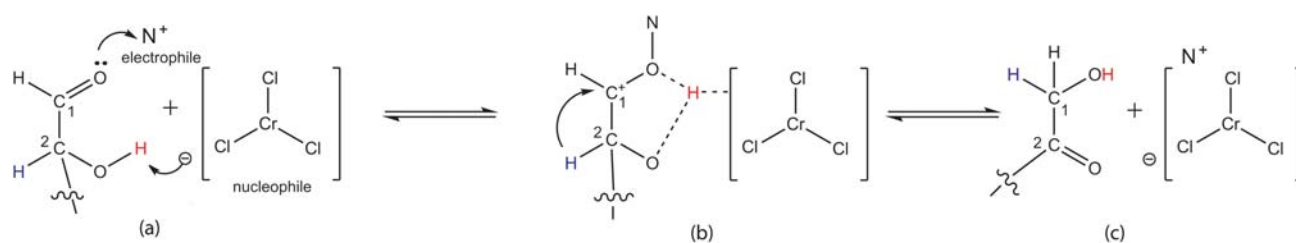
### 2.2.2 Glucose–fructose isomerisation in non-aqueous media.

The above analysis underscores the place of concerted catalysis in achieving high fructose selectivity in the isomerisation of glucose in aqueous media. Extension of the same principle can be used to account for the same reaction in non-aqueous media. The acid–base bifunctionality of the catalyst or enzyme in aqueous medium is replaced with nucleophilicity–electrophilicity in non-aqueous media. Hence, the suggested isomerisation of glucose to fructose *via* hydride shift in the EMIM<sup>+</sup>Cl<sup>−</sup>/CrCl<sub>2</sub> system can be rationalized by concerted catalysis. Using the acyclic structure of glucose, the electrophile in the cation of the ionic liquid (the cation of the complex, EMIM<sup>+</sup>), activates the substrate (glucose) at the carbonyl carbon C<sub>1</sub>. There are two nucleophiles in the system Cl<sup>−</sup> and [CrCl<sub>3</sub>]<sup>−</sup>. The chloride ion is more basic than [CrCl<sub>3</sub>]<sup>−</sup>, since the negative charge on [CrCl<sub>3</sub>]<sup>−</sup> is not readily available for basic interaction due to resonance effects, it behaves like a charge-neutral species with a very small dipole moment.

The [CrCl<sub>3</sub>]<sup>−</sup> interacts with the hydroxide group at the C<sub>2</sub> of the substrate to facilitate a proton transfer to C<sub>1</sub>. This simultaneous activation of the substrate C<sub>1</sub> (glucose) promotes a hydride shift from C<sub>2</sub> to C<sub>1</sub> to form the ketose product (fructose) [see Scheme 5]. The fructose is then subsequently dehydrated *via* concerted catalysis to HMF as explained earlier in Scheme 4.

The chloride ion is less suitable as a facilitator of proton transfer because of its basicity. It tends to hold on to the proton too strongly to allow the proton transfer from C<sub>2</sub> to C<sub>1</sub>. This accounts for the low reactivity of glucose in ionic liquid systems without CrCl<sub>2</sub>. A similar explanation is suggested for the inability of BMIM<sup>+</sup>Cl<sup>−</sup> to convert glucose to HMF as reported by Qi *et al.*<sup>22</sup> However, glucose and related disaccharides were observed to be effectively converted to HMF in BMIM<sup>+</sup>Cl<sup>−</sup>/CrCl<sub>3</sub>. The nucleophile here is [CrCl<sub>4</sub>]<sup>−</sup>. Using the principle of resonance, [CrCl<sub>4</sub>]<sup>−</sup> can also be assumed to have a very small dipole moment.

**2.2.3 Glucose to HMF in non-aqueous media.** Although Zhang *et al.*<sup>23</sup> suggested that a chromium enolate may be the key intermediate in the catalyst action of the EMIM<sup>+</sup>Cl<sup>−</sup>/CrCl<sub>2</sub> system, however, the authors did not provide evidence to support their suggestion. Also the suggestion could not be extrapolated to account for similar catalytic effects observed in other systems where chromium salts or other metal salts are absent. For example, a system consisting of an ionic liquid and NHC–Cr (a heterocyclic carbene), a strong nucleophilic carbene catalyst was reported to exhibit excellent capacity for efficient and selective conversion of fructose and glucose to HMF.<sup>35</sup> A yield of 96% at 80 °C and 84% at 100 °C were obtained using fructose and glucose respectively. The unprecedented performance of this system can be rationalized in terms of concerted catalysis. The carbene precursor catalyst (NHC–Cr) interacts with part of the ionic liquid to generate the carbene which can be coupled with the ionic liquid cation (electrophile) to promote selective isomerisation of glucose to fructose as well as dehydration of fructose to HMF *via* concerted catalysis. Other carbene precursors that do not contain metals *e.g.* thiamine have the potential to display the same or similar catalytic effects.



————— covalent bond

----- partial covalent bonding

(a) Concerted activation of the substrate by nucleophile and electrophile

(b) Proton transfer and hydride shift intermediate complex

(c) Ketose product

**Scheme 5** Isomerisation of glucose to fructose in non-aqueous medium *via* concerted catalysis.



Furthermore, according to Dumesic *et al.*<sup>24</sup> a biphasic system of a DMSO-modified aqueous phase and dichloromethane (DCM) affords an HMF yield of 53% in the dehydration of glucose in the absence of acid catalyst. As suggested earlier, DCM acts as a nucleophile to lower the temperature of dehydration of fructose to HMF by its participation in concerted catalysis. Again, the glucose is the substrate in the same system and the possibility of glucose isomerisation cannot be ruled out. The chloride atoms in DCM may facilitate a proton transfer in a similar manner to the chloride atoms in  $[\text{CrCl}_3]^-$  to promote the glucose isomerisation to fructose. Then the resulting fructose is further dehydrated to HMF through concerted catalysis.

### 2.3 Production of HMF from glucose and polysaccharides

The use of polysaccharides as the substrate for the production of HMF holds the advantage of availability and lower cost as the raw material in the future biorefinery. Efficient and selective conversion of polysaccharides especially cellulose are most desirable because of its abundance and because it is a non-food material. Starch and cellulose are made up of glucose units in the pyranose form. In starch, the pyranose rings are bonded *via*  $\alpha$ -1,4-glycosidic linkages arranged in a helical structure such that the  $\alpha$ -1,4-glycosidic linkages are easily accessible by chemicals and enzymes. However, in cellulose the pyranose rings are bonded *via*  $\beta$ -1,4-glycosidic linkages which gives a chain side-by-side arrangement. This arrangement favoured extensive intra- and inter-chain hydrogen bonding between the groups near the glycosidic bonds. Thus, the glycosidic bonds are not as readily accessible to reagents as those in starch. Therefore, the first hurdle at making cellulose chemically sensitive is the disruption of its network of hydrogen bonds. This entails solubilisation or depolymerisation of cellulose in pre-treatment reagents or systems that completely break or weaken the hydrogen bonds. Thus, the conversion of cellulose to HMF may involve three chemical processes, namely: hydrolysis, isomerisation and dehydration. A two-unit process operation could be envisaged which would consist of a hydrolysis unit and the glucose-to-HMF unit, since direct conversion of glucose to HMF has been demonstrated to be possible. In addition to these two chemical process units, a glucose and HMF isolation or purification unit may be required. But one-step conversion of cellulose to HMF will reduce the process units to two, cellulose-to-HMF and HMF isolation or purification units.

One-step conversion of cellulose to HMF has been shown not only to be feasible but has also been demonstrated. This is because most ionic liquid reaction systems for conversion of glucose to HMF can sufficiently solubilise cellulose and hydrolyse cellulose in the presence of acid catalysts. Acidic ionic liquids can act as both solvent and catalyst. Examples of systems for direct conversion of cellulose to HMF are presented in Table 3.

From the results in Table 2, it is clear that the chloride ion is common to all the systems. It shows that the chloride ion is crucial to the dissolution of cellulose in the systems. The extent of solubilisation of cellulose can then be said to be a function of chloride ion concentration in the systems. The charge-neutral nucleophile components (in entries 2, 3, 4 & 5) are very similar but their electrophiles are different. So the yield of HMF and the efficiency of these systems can be attributed to the abilities of the

**Table 3** Direct conversion of cellulose to HMF

Solubilisation of cellulose (disruption of the hydrogen bond network)		Cleavage of the $\beta$ -1,4-glycosidic bond		Isomerisation of glucose to fructose via concerted catalysis			Reaction condition	HMF yield	Ref.
Reaction system	Solvent	Hydrolysis agent	Charge-neutral nucleophile	electrophile	Charged nucleophile				
1	$\text{LiCl-HCl-CH}_2\text{Cl-CH}_2\text{Cl}$	$\text{LiCl-HCl}$	$\text{HCl}$	$\text{CH}_2\text{Cl-CH}_2\text{Cl}$	$\text{Li}^+, \text{H}^+$	$\text{Cl}^-$	65 °C, 18–30 h	71%	36
2	$[\text{EMIM}][\text{Cl}]-\text{CrCl}_2-\text{CuCl}_2$	$[\text{EMIM}][\text{Cl}]$	$\text{HCl}$	$\text{CrCl}_2-\text{CuCl}_2$	$[\text{EMIM}]^+$	$\text{Cl}^-$	80–120 °C	55.4%	37
3	$\text{DMA-LiCl-HCl-}[\text{EMIM}][\text{Cl}]-\text{CrCl}_2$	$\text{DMA/LiCl (10\%)}, [\text{EMIM}][\text{Cl}]$	$\text{HCl}$	$\text{CrCl}_2$	$[\text{Li}(\text{DMA})]^+$	$\text{Cl}^-$	140 °C, 2 h	54%	38
4	$[\text{AMIM}][\text{Cl}]-\text{CrCl}_2$	$[\text{AMIM}][\text{Cl}]$	$[\text{EMIM}][\text{HSO}_4^-]$	$\text{CrCl}_2$	$[\text{AMIM}]^+$	$\text{Cl}^-$	100 °C, 6 h	50%	39
5	$[\text{BMIM}][\text{Cl}]-[\text{EMIM}][\text{HSO}_4^-]-\text{CrCl}_2$	$[\text{BMIM}][\text{Cl}]-[\text{EMIM}][\text{HSO}_4^-]$	$[\text{EMIM}][\text{HSO}_4^-]$	$\text{CrCl}_2$	$[\text{BMIM}]^+$	$[\text{EMIM}]^+$		<13%	40

electrophile to couple with their respective nucleophile in concerted catalysis of glucose to HMF. The lower yield of HMF in entry 5 could be attributed to inaccessibility of the charge centre in [BMIM] to the glucose due to steric effects. The system in entry 1 gives the highest HMF yield, but it is the least efficient considering its duration. The system does not give HMF directly but 5-(chloromethyl)furfural (CMF). CMF is hydrophobic, and although not itself a biofuel candidate, can be readily combined with ethanol to yield ethoxymethylfurfural, a suitable fuel candidate compound. The chemical reactions involved here can be analysed as follows: solubilisation of the cellulose in LiCl and hydrolysis with HCl; the absence of water will yield chlorinated glucose. The chlorinated glucose is then isomerised and dehydrated to HMF in 1, 2-dichloroethane in the presence of more LiCl/HCl. The three reagents, LiCl, HCl and 1, 2-dichloroethane supply the catalytic species required for the direct conversion of cellulose to HMF.

From the above analyses, it clearly shows that the ionic liquid systems have the potential to make the goal of producing biofuels and biorefining competitive with fossil-derived fuels and petroleum refining respectively. However, the economic feasibility of the system is a function of the cost and efficiency of the ionic liquids for dissolution of cellulose. This efficiency is judged in terms of the extent of dissolution and the solubilisation temperature of cellulose in the ionic liquid. It has been suggested that for efficient processing of cellulose biomass, no extra energy (for example heating) should be necessary in order to reduce the energy cost.<sup>41,42</sup> The ability of ionic liquids to dissolve cellulose under mild conditions and the solubilisation temperature of cellulose appears to be linearly related to the viscosity of ionic liquids. Most of the common ionic liquids for dissolving cellulose are based on chloride salts which suffer from the disadvantage of high melting point and high viscosity. However, new classes of polar ionic liquids have been found to have lower melting points and viscosities than the chloride salt based ones. They are based on carboxylate salts and dimethylphosphate salts.<sup>43</sup> The formate salts of 1-ethyl-3-methylimidazolium, [EMIM] cation and 1-allyl-3-methylimidazolium [AMIM] cation were found to have lower viscosities than the corresponding chlorides salts. Cellulose was reported to dissolve in high concentration in 1-allyl-3-methylimidazolium formate ([AMIM][HCOO]<sup>-</sup>) under mild conditions. The formate-based ionic liquids have the drawback of poor thermal stability. On the other hand, [EMIM][(MeO)(Me)(PO<sub>2</sub>)] was reported to be thermally stable up to 260–290 °C and have viscosity values between 100–500 cP at 25 °C. The viscosity values are much lower than that of the chloride salts. The higher capacity of these ionic liquids to dissolve cellulose was attributed to their higher hydrogen bonding basicity over the chloride-based ones. Also the solubilisation temperatures of cellulose depend on the structure of the anions of the ionic liquid. It is expected that the use of these new ionic liquids will make possible higher yields of HMF in the direct cellulose-to-HMF process. But the acid test for the ionic liquids will be their suitability for the conversion of glucose to HMF.

In summary, the concerted catalysis principle was used to rationalise the conversion of common hexose substrates (fructose and glucose) to HMF in non-aqueous systems. The successful transformation required readily accessible nucleophiles and electrophiles. Two kinds of nucleophiles were identified, strongly

charged nucleophiles that have high net dipole moments and charge-neutral nucleophiles that have very low values of net dipole moment. Conversion of glucose to HMF is *via* initial isomerisation to fructose before subsequent dehydration to HMF. The initial isomerisation step required the pairing of an electrophile and a charge-neutral nucleophile, however, fructose dehydration can be catalysed by both categories of nucleophiles. Addition of acid catalysts into ionic liquid systems that can efficiently convert glucose to HMF were shown to be suitable for the direct conversion of cellulose to HMF.

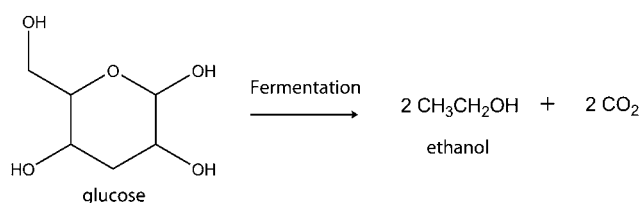
### 3. Transportation fuels or fuel intermediates from HMF and furfural

In this part of the paper, we examine efforts at transforming HMF and furfural to transportation fuels or fuel intermediates. We also discuss the conversion of HMF to a gasoline fuel and the need to increase the carbon chain length of HMF in order to obtain kerosene and diesel-range fuel intermediates. We appraise the updated strategies that have been employed in this respect and we suggest more potential reaction routes for obtaining kerosene and diesel-range fuel intermediates from HMF.

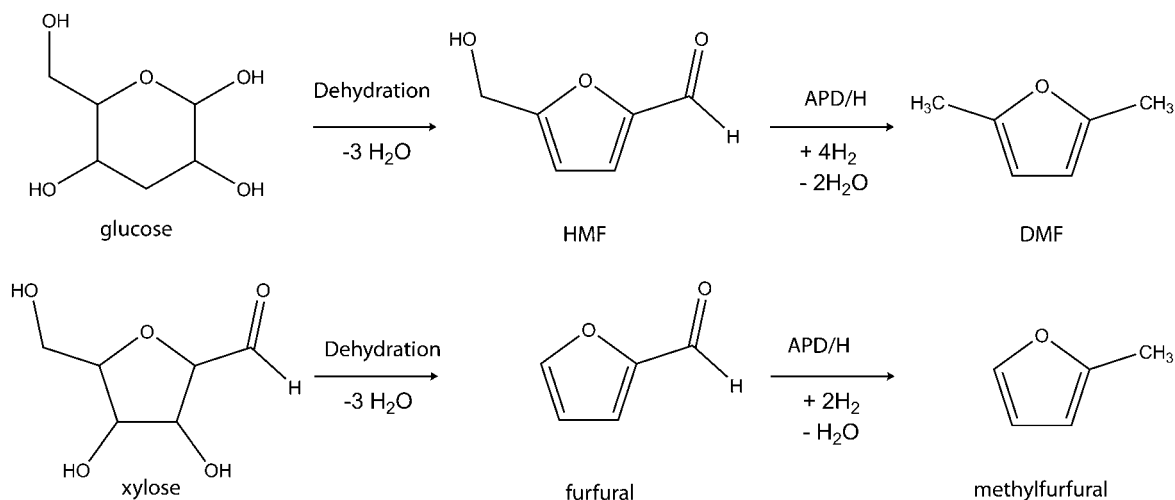
#### 3.1 Gasoline-range fuel from HMF and furfural

For a long time, lower alcohols (ethanol and butanol) were the prominent biofuels produced from carbohydrate biomass (Scheme 6). These biofuels are based on slow biochemical reactions and energy-demanding distillation processes which have generated numerous questions about the efficiency of their production.<sup>42,43</sup>

However, in recent times the range of biofuels obtainable from carbohydrate biomass has increased considerably. Part of these efforts is being championed by Dumesic and his co-workers.<sup>44</sup> The group has demonstrated the possibility of producing hydrogen and hydrocarbons from carbohydrates and simple polyols. The process for producing hydrogen and hydrocarbons involves aqueous phase reforming (APR) and aqueous phase dehydration and hydrogenation (APD/H) respectively.<sup>44–47</sup> The reactions opened up prospects of producing new varieties of chemicals and biofuels exclusively from carbohydrates. Among several efforts, Dumesic and co-workers demonstrated the strategies for the conversion of carbohydrate-based biomass to hydrocarbon (*e.g.* conversion of sorbitol to hexane) *via* aqueous-phase dehydration, hydrogenation and hydrogenolysis reactions. The conversion is achieved in a one-pot process with the use of a four-phase reactor. Oxygen removal through dehydration and hydrogenation transforms the hydrophilic substrate into a hydrophobic product with drastically reduced aqueous-phase



**Scheme 6** Biochemical conversion of glucose to ethanol.



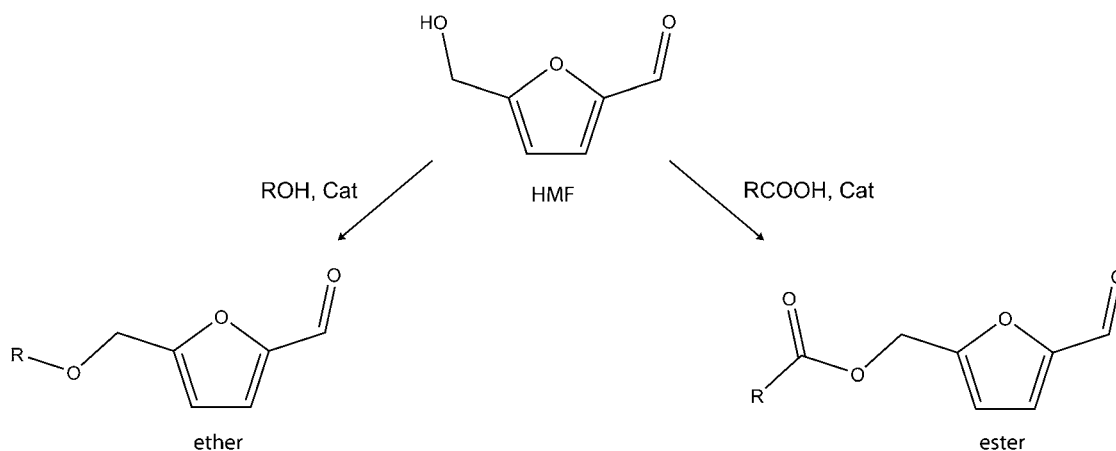
**Scheme 7** Chemical conversion of glucose to DMF and xylose to methylfurfural analogue.

solubility. The hydrophobic product readily separates out from the aqueous reaction system. These strategies afford about 90% of the energy of the carbohydrate and  $H_2$  feeds.<sup>46–48</sup> These strategies lay the platform for the conversion of other carbohydrate substrates to hydrocarbons and new biofuel varieties. One of the applaudable contributions of Dumesic's group is the production of 2,5-dimethylfuran (DMF) from fructose *via* a two-step process.<sup>49</sup> The fructose was dehydrated to HMF which was subsequently hydrogenolysed to DMF (Scheme 7).

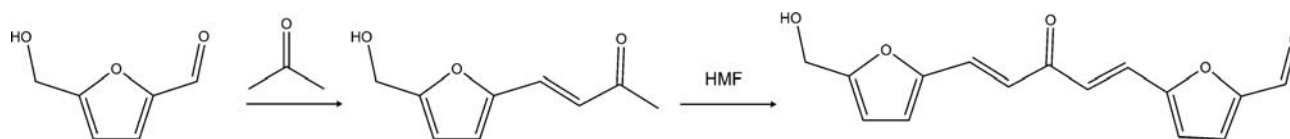
DMF has properties that are similar to current petroleum-based gasoline fuels and it is considered to be a suitable substitute or fuel additive for petrol engines due to its high octane number. It is also adjudged a better fuel than ethanol in terms of production efficiency, energy density, handling and storage.

### 3.2 Existing approaches to kerosene and diesel-range fuel intermediates from HMF and furfural

Kerosene and diesel are other important transportation fuels. These fuels have carbon chains and properties that are not met by hydrocarbons obtainable from one molecule of HMF or furfural. Thus, the production of diesel-range fuels based on the strategies described above will require self-condensation of two or more HMF or furfural molecules or their cross-condensation with other compatible compounds that are derived from renewable feedstocks. The success of this new task will require intelligent use of the intrinsic functionality already present in intermediates. The functionalities of these intermediates are  $-OH$  group,  $-CO$  group and the five-membered ring heterocyclic aromatic system. HMF has these three functionalities but the



**Scheme 8** Formation of alkoxyethylfurfural ethers and esters.



**Scheme 9** Cross-aldol condensation of HMF with acetone.

–OH group is absent in furfural. With these functionalities, HMF and furfural can undergo several self- and cross-condensation reactions. A superficial survey of the literature reveals that most of the reports on the formation of diesel-range fuel intermediates focus on cross-condensation approaches. The approaches involve the use complimentary feedstocks in order to extend the carbon chain of the resulting intermediates or bio-fuels. The cross-condensation strategies are discussed below.

**3.2.1 Cross-condensation of HMF (non C–C coupling).** A recent patent report on the formation of diesel-range biofuels describes a new family of furan derivatives in which lower alcohols and corresponding carboxylic acids are condensed with HMF through the –OH group. The condensation products are alkoxy-methylfurfurals ethers and esters respectively (see Scheme 8). These new furanics have to their credit good oxidation stability, high cetane number and excellent miscibility with petrol diesel. The reaction is catalysed by either conventional mineral acids or solid acids and can be achieved in a single-step process directly from glucose–alcohol or glucose–carboxylic acid mixtures.<sup>50</sup>

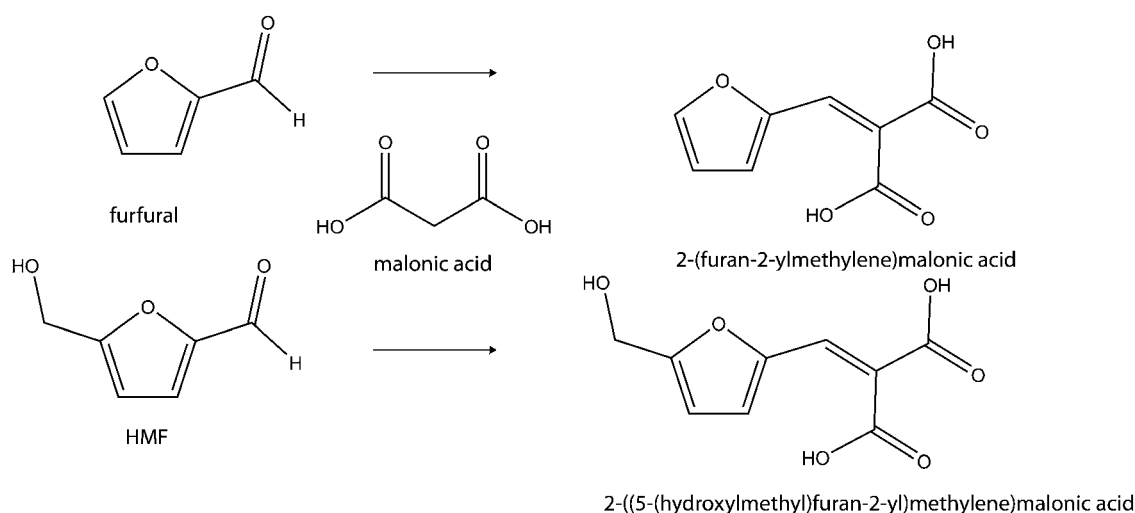
**3.2.2 Cross-condensation (cross-coupling) of HMF and furfural.** Other attempted efforts at producing diesel-range fuels from carbohydrate biomass have been reported by Dumesic and co-workers<sup>51</sup> by considering aldol condensations. HMF is not a candidate for self-aldol condensation as it lacks an  $\alpha$ -hydrogen atom but its hydrogenated derivative (furan) is a suitable candidate. On the other hand, HMF can undergo cross-condensation with acetone (and other aldehydes and ketones with at least an acidic  $\alpha$ -proton). The cross-aldol condensation route has been demonstrated by Dumesic and co-workers as an equally probable option for producing diesel-range biofuels (see Scheme 9).<sup>51–53</sup>

In a similar carbanion reaction, malonic acid, an activated methylene compound that can be derived from biomass was suggested as a suitable coupling partner with HMF. Here, the malonic acid can link furfural or HMF by C–C bond formation *via* a Knoevenagel reaction, giving (C<sub>8</sub> and C<sub>9</sub>) biofuel intermediates respectively (see Scheme 10).<sup>54</sup>

The resulting compounds in Schemes 9 and 10 are not fuels but fuel intermediates. They are rich in oxygen and will be hydrophilic. Subsequent hydrogenolysis is required to eliminate as much oxygen as possible to reduce the hydrophilicity to an acceptable level as in the case of HMF to DMF. Or complete elimination and saturation to yield the corresponding alkanes.

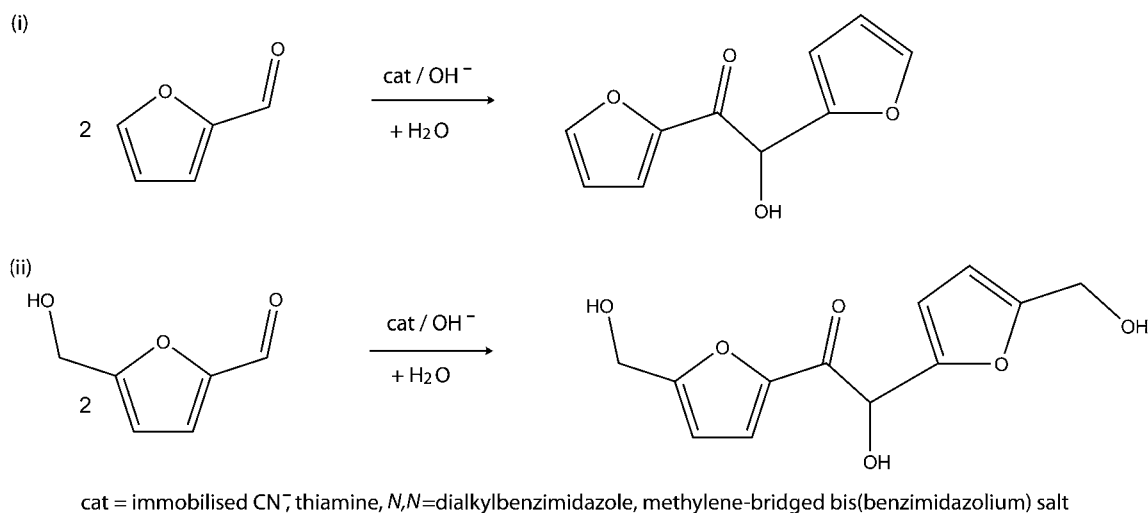
### 3.3 New strategies to kerosene and diesel-range fuel intermediates from HMF and furfural

The approaches described above for the production of kerosene and diesel-range fuel intermediates from HMF and furfural are viable routes in terms of reaction conversions and selectivities. However, the complimentary feedstocks (ethanol, acetone, ethanoic acid, malonic acid *etc.*) engaged in these processes may not be exclusively from renewable sources, or they may suffer from energy balance limitations inherent in their production methods. The need for complimentary feedstocks can be avoided if there are efficient reaction routes for self-condensation of HMF or furfural through the use of the same or alternative functionalities of these fuel intermediate molecules. That is, a reaction route that can link two furfurals or HMFs through their –OH groups, two HMFs through their –CO groups and two or more HMFs through the reaction between the –CO group of one with the –OH group of another. Such reactions can lead to kerosene and diesel-range fuel intermediates that are not only obtained from single starting carbohydrate feedstocks but also from exclusively renewable sources. Within the limit of available evidence from the literature, there have yet to be any reports on the production of kerosene and diesel-range fuel intermediates that are based on self-condensation of HMF or furfural. The potential reaction routes for achieving this goal include: the benzoin reaction, the hetero Diels–Alder reaction, condensation of furfurylic alcohol and ketonisation reactions. It is important to add that the resulting compounds from the C–C coupling of HMF molecules may not be suitable for use as fuels directly. Subsequent hydrogenolysis will transform them into fuels of kerosene and diesel-range in the same manner as products in the cross-coupling approach. Below are the highlights of the



**Scheme 10** Cross-condensation of HMF and furfural with malonic acid through the Knoevenagel reaction.





**Scheme 11** Self-condensation of (i) furfural and (ii) HMF, *via* the benzoin reaction.

proposed reaction routes for the self-condensation of HMF and furfural.

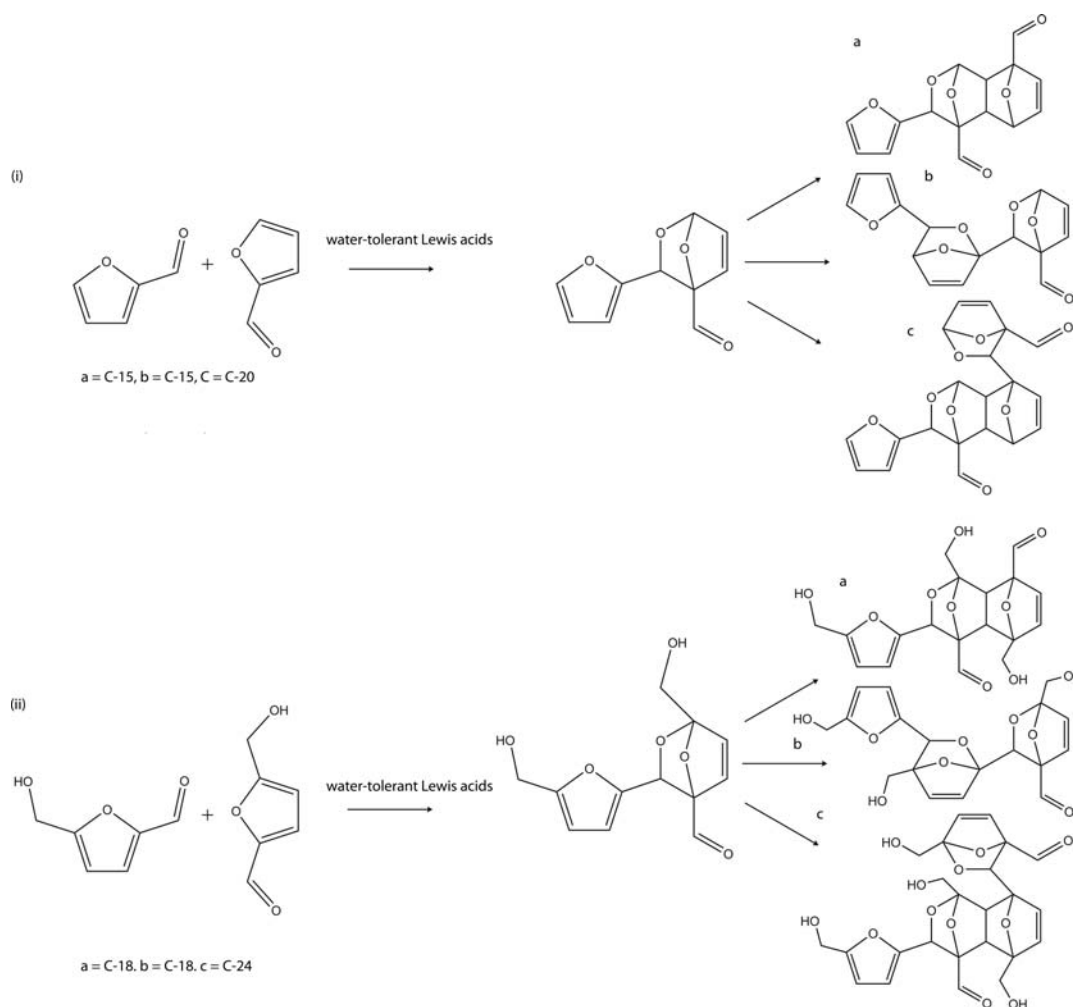
**3.3.1 Benzoin condensation.** Furfural and HMF are aromatic aldehyde compounds. One of the well documented condensation reactions of aromatic aldehydes is the benzoin condensation. The reaction links the carbonyl carbons of aromatic aldehydes *via* a C–C bond to form a hydroxyl ketone product called aryoin.<sup>55</sup> Similarly, the self-benzoin condensation of HMF forms a coupled product called fuoin. This reaction is catalysed by  $\text{CN}^-$ , thiamine or thiazolium salts and benzimidazolium salts in organic solvents (Scheme 11).<sup>56–66</sup> It has been demonstrated that the reaction can take place in aqueous media under mild conditions when the catalyst is immobilized on solid supports. In spite of the feasibility of this route to diesel-range fuel intermediates from HMF or furfural, it has not been considered for the same purpose. Since, imidazolium based ionic liquids are employed for conversion of glucose and cellulose to HMF, and benzoin condensation can be promoted by  $\text{CN}^-$ , thus a system made up of imidazolium cations and  $\text{CN}^-$  anions could afford direct formation of a  $\text{C}_{12}$  or  $\text{C}_{10}$  intermediate from glucose or xylose respectively. The  $\text{C}_{12}$  or  $\text{C}_{10}$  intermediate can then be transformed to the respective hydrocarbons or other compounds that have suitable fuel properties.

**3.3.2 Hetero Diels–Alder reaction.** Another possible reaction route for linking two or more HMF units together by C–C bond formation is the Diels–Alder reaction. This reaction route is yet to receive consideration for the formation of  $\text{C}_{12}$  biofuel intermediates. A typical Diels–Alder reaction is one of the most important methods used to form cyclic structures and it is reported to be one of the earliest examples of C–C bond formation reaction in aqueous media. A typical Diels–Alder reaction is a  $4\pi_s + 2\pi_s$  reaction involving a diene and a dienophile in which all atoms participating in the reaction are unsaturated carbons.<sup>65</sup> Interestingly, the Diels–Alder reaction also enjoys rate acceleration and enhanced selectivity in aqueous solution. This is attributed to the combined effects of hydrogen bonding of the water and enforced hydrophobic interactions.

Rationalising this in terms of transition state theory, it has been explained that hydration raises the energy of the initial state more than the transition state and hydrogen-bonding interaction stabilizes the transition state more than the initial state. The highly polarisable and saturated complex plays a key role in the two effects.<sup>66</sup> There is no formal restriction on the nature of the atoms in this type of reaction, since it is the electrons in the  $\pi$ -bonds that are reacting, therefore the  $\pi$ -bond of the carbonyl group in HMF can act as the dienophile. Diels–Alder reactions have been found to be particularly efficient and rapid when the dienophile and diene contain one or more electron-withdrawing groups and electron-releasing groups respectively.<sup>67</sup>

The reactivity of furan-based compounds as dienes is low because of their aromatic character, however, a number of [4 + 2] reactions involving furan have been reported in the literature. Although, Diels–Alder reactions can proceed without the need for catalysts, the reactions are slow and need to be accelerated by physical methods such as high pressure, high temperature or ultrasound ionisation. Also, Diels–Alder reactions are greatly enhanced by Lewis acid catalysis. Lewis-acid-catalysed Diels–Alder reactions proceed by coordinating to the activating group of the dienophile (for normal electron-demand Diels–Alder reactions), thereby lowering the LUMO dienophile–HOMO diene energy gap and accelerating the reaction. Specifically, Hafnium compounds have been identified as a suitable Lewis acid which provide the Diels–Alder reactions of furan in good yield.<sup>68,69</sup> Other Lewis acids that are air stable and water tolerant have also been reported for the Diels–Alder reaction of furan with suitable dienophiles.<sup>70–72</sup>

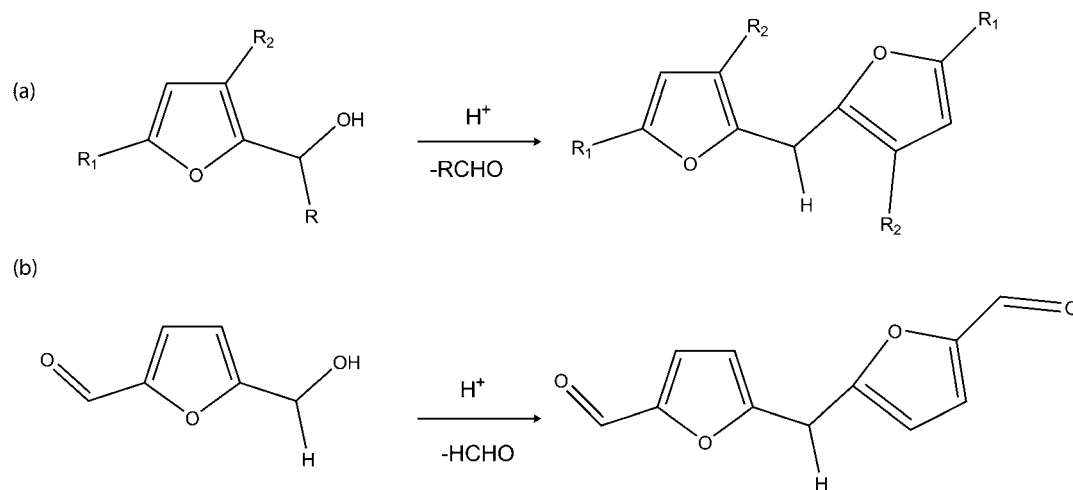
The above highlight can be said to have established the platform for the application of Diels–Alder reactions for the formation of  $\text{C}_{12}$ -biofuel intermediates exclusively from HMF. A  $\text{C}_{12}$  or  $\text{C}_{10}$  biofuel intermediate can be formed *via* the hetero Diels–Alder condensation of two HMF or furfural molecules respectively with a furan ring as the diene and the carbonyl group as the dienophile. Successive condensations of more than two units of HMF and furfural are also possible giving six- and five-carbon chain multiples of biofuel intermediates. Normal homogenous Lewis acid catalysts required to activate a carbonyl



**Scheme 12** Proposed hetero Diels–Alder condensation of (i) furfural and (ii) HMF.

group containing a dienophile are faced with the problem of their use in excess. The process can be made greener by heterogenising the Lewis acid catalyst. This will also afford the advantage of the heterogeneous catalysts in the reaction in terms of operational simplicity, ability to be filtered and reusability.<sup>65</sup>

**3.3.3 Condensation of furfurylic alcohols.** The hydroxyl group of HMF can also be exploited for C–C bond formation for linking two HMF units to form longer chain length biofuel intermediates. HMF is a perfumed alcohol and self-condensation of furfuryl alcohols has been reported as a useful and interesting

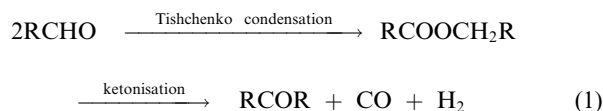


**Scheme 13** (a) Condensation of furfuryl alcohol. (b) Proposed acid condensation of HMF.

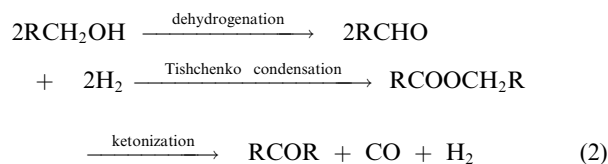
method for the synthesis of symmetric bis(2-furyl) methanes. Acid-promoted oligomerisation reactions of furfuryl alcohols are reported to be characterised by the formation of mixtures of products, in which bis(2-furyl) methane has been isolated in low yield. The acids used in some of the reactions include: polyphosphoric acid, silver(I) ions, and trichloroacetic acid in polar organic solvents such as methanol at high temperature.<sup>73,74</sup> In the search for new approaches and better reaction conditions for the preparation of symmetric bis(2-furyl) methane, Tatyama *et al.*<sup>75</sup> came up with new methods that are simple under mild conditions with good product yields. The reaction in Scheme 13 was carried out in dioxane in the presence of a catalytic amount of concentrated HClO<sub>4</sub> at temperatures below 100 °C. Tris(2-furyl) methane was also prepared from the reaction of 5-substituted 2-furaldehydes with ethylene glycol in the presence of strong acids using benzene as the solvent.

The reactions in the Scheme 13 can be well adapted for the formation of C<sub>11</sub> biofuel intermediates from HMF. Although, the atom economy in these reactions are lower when compared to that of the Diels–Alder condensation approach, the percentage carbon utilisation of biofuel intermediates is still reasonably high (91.7%) for the commercial production of diesel-range biofuel intermediates from HMF. In order to have an overall green process, the use of an immobilised, hydrophilic, strong Brønsted acid ionic liquid is suggested. The hydrophilic nature of the ionic liquid will allow close interaction of the acid site with the substrate, at the same time, the immobilisation will afford reusability of the acid and easy isolation of the product. This arrangement will not only make the process environmentally friendly but also afford intensification and optimisation of the catalyst and the solvent.

**3.3.4 Tishchenko and ketonisation reactions.** One more alternative for linking two or more HMF or furfural units together *via* C–C bond formation is through consecutive Tishchenko condensation and ketonisation reactions (Schemes 14 and 15). The Tishchenko reaction is a disproportionation reaction that allows the formation of an ester from two equivalent aldehydes lacking an  $\alpha$ -hydrogen.<sup>76</sup> The condensation reaction is usually catalysed with an alkoxide or a Lewis acid.<sup>77–79</sup> Ketonisation of the resulting ester will give a ketone.<sup>80</sup>

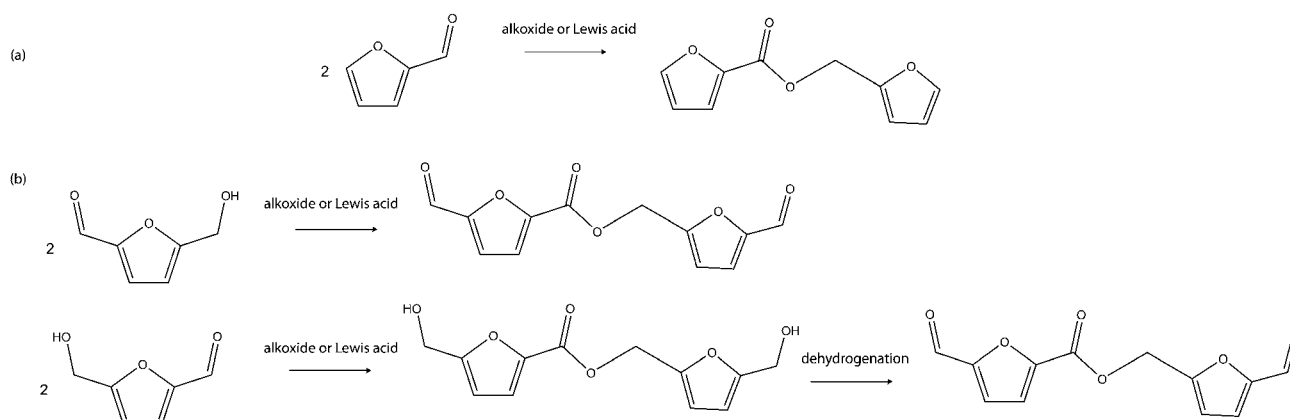


The ketone products will contain one carbon atom fewer than the number of carbon atoms in the substrate. The possibility of primary alcohol dehydrogenation with subsequent ketonisation had also been reported.<sup>81–84</sup> The reaction has been found to proceed consecutively with the formation of aldehydes and esters as intermediates. Aldehydes and esters are the major products at lower temperatures while ketones are the predominant product at higher temperatures.<sup>84</sup>

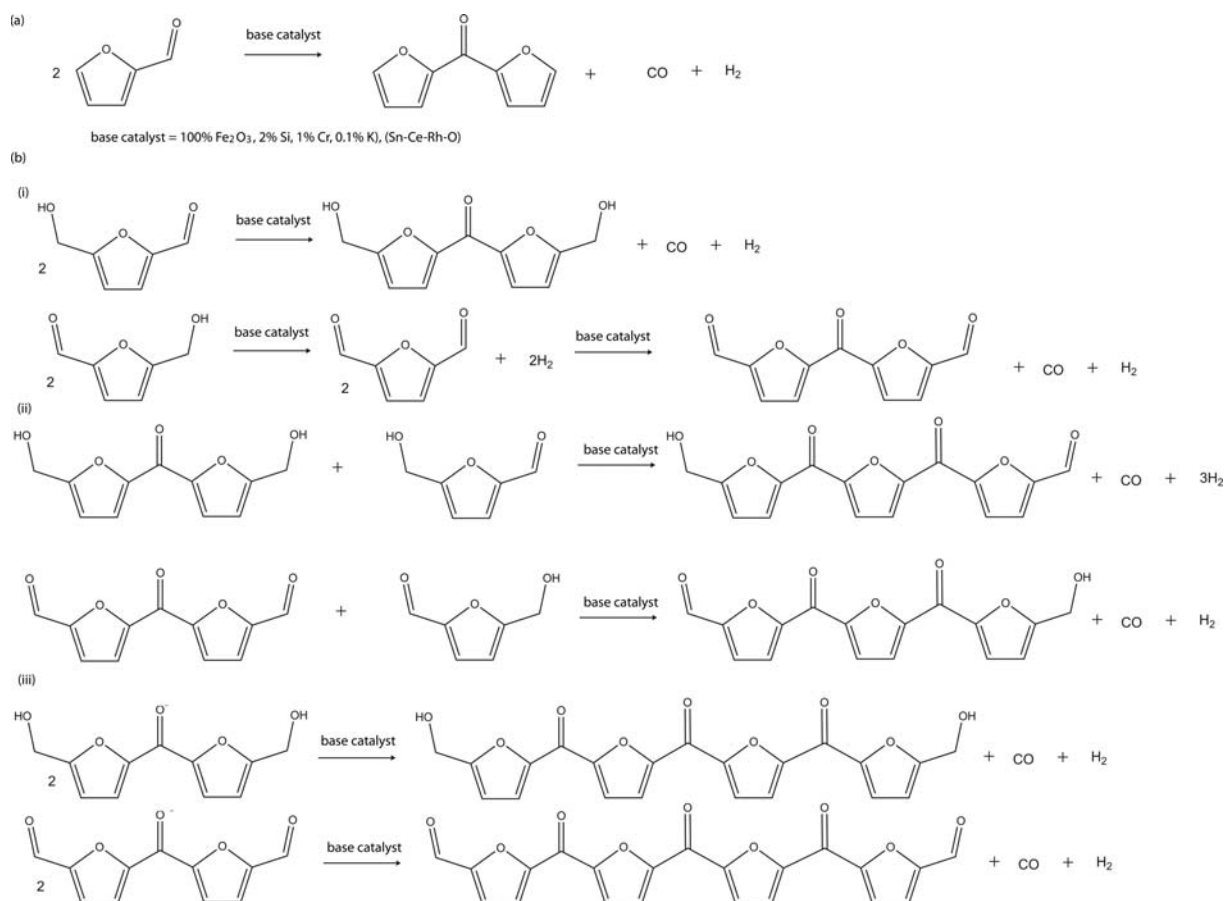


Furfural and HMF lack  $\alpha$ -hydrogens to their carbonyl groups, HMF in addition has a primary hydroxyl group. They satisfy the functionality pre-requisite, hence, they are qualified as substrates for the transformation described above. Therefore, this unique reaction and catalysts can be extrapolated for the formation of longer carbon chain biofuel intermediates from furfural and HMF. The Tishchenko condensation of furfural and HMF may be sufficient enough to obtain the desired fuel product, provided the ester products have acceptable fuel properties (such as stability to oxidation, high cetane number, hydrophobicity *etc.*) like the alkoxyethylfurfural esters and ethers. Otherwise, the C–C linkage *via* ketonisation of the esters then becomes necessary to give the ketone product (fuel intermediate).

It has been showed that low acid–base activity of the catalyst is essential to the selectivity of the catalyst to ketone formation and also to minimise competitive side-reactions such as dehydration to alkene and ether formations. In line with this fact, iron oxide catalyst (100%Fe<sub>2</sub>O<sub>3</sub>, 2%Si, 1%Cr, 0.1%K) and ternary catalyst (Sn–Ce–Rh–O) have been found to have high ketonisation activities and selectivities for the reaction. Furfural and HMF contain at least one of the required functional groups for the ketonisation reaction, hence, their bimolecular condensation is



**Scheme 14** Proposed Tishchenko condensation of (a) furfural and (b) HMF.



Scheme 15 Proposed ketonisation reactions of (a) furfural and (b) HMF.

expected to give C<sub>9</sub> and C<sub>11</sub> ketone products from furfural and HMF respectively. Furfural has just one of the required functional groups, an aldehyde group, hence, its bimolecular condensation is expected to give only the C<sub>9</sub> ketone product. However, HMF has two functional groups, an aldehyde and a hydroxyl group, that can be engaged for the ketonisation process, multiple condensations are therefore possible in addition to the starting C<sub>11</sub> ketone produced *via* a one stage bimolecular condensation like furfural. Thus, a C<sub>16</sub>, C<sub>21</sub>, C<sub>26</sub>, C<sub>31</sub>,... series of di, tri, tetra, penta,... ketone products is envisaged when HMF is the starting substrate.

Another important aspect of the application of the ketonisation reaction route for the production of longer carbon chain biofuel intermediates from HMF and furfural is the fact that ketone formation occurs in the gas phase at high temperatures. This is in contrast to the other self-condensation reaction routes suggested above as well as other cross-condensation reaction routes that have been explored for the same purpose where the reactions are carried out in the liquid phase. In those reaction routes, the reaction mixture HMF and furfural formation processes can be used directly without isolating them from their solution. In contrast, self-condensation by ketonisation will require the use of HMF and furfural in their pure forms. This places a demand of adopting HMF and furfural production routes from carbohydrate sources that enable the easy isolation at a reasonably high level of purity. An example of an HMF

production route was reported by Hu *et al.*<sup>84</sup> The process involves the conversion of fructose to HMF in an ethyl acetate/renewable ionic liquid (IL) biphasic system. The phase separation between the ethyl acetate and the renewable ionic liquid was shown to have no cross-contamination such that the renewable (IL) can be reused. In the same vein, the ethyl acetate containing the HMF product can be easily distilled from HMF and reused. This process affords a green process for the formation of HMF at a high level of purity. Therefore, the integration of this green process for the formation of HMF with the ketonisation reaction would enable another environmentally friendly process for the formation of longer carbon chain biofuel intermediates.

#### 4. Conclusion

The production of transportation fuel from biomass is a worldwide strategy towards the reduction of CO<sub>2</sub> emission from the continuous combustion of fossil fuels. This goal will naturally be actualised when the cost of producing biofuels is on a par with or cheaper than fuels from fossil sources. HMF and furfural are the key carbohydrate-derived intermediates for future biorefining. Hence, their efficient production from cheap and readily available feedstocks is paramount for achieving the goal of making biofuels economically competitive with fossil-derived fuels. Established processes for the production of HMF and furfural are based on fructose which is expensive and not readily



available. Recent process developments in using readily available feedstocks (glucose and cellulose) for HMF and furfural production focused on non-aqueous homogenous catalytic processes. Efforts at producing diesel-range biofuels from carbohydrate biomass have focused on the cross-condensation of HMF or furfural with other lower carbon chain alcohols, carboxylic acids, aldehydes or ketones. The challenge envisaged here is that the feedstock for these processes may not be exclusively from renewable sources or it may have the disadvantages of poor energy balance inherent in the production of the co-reactants of the intermediates from renewable sources. Despite the availability of potential reaction routes for self-condensation of HMF and furfural from base organic chemistry, a superficial review of the literature reveals no effort in this direction. Therefore, four potential reaction routes (Schemes 11–15) which are yet to be exploited for the self-condensation of HMF and furfural were suggested and highlighted.

## Acknowledgements

Olusola O. James is grateful to TWAS and CSIR (India) for a TWAS-CSIR Postgraduate Fellowship Award. James is also thankful to Prof. K.O. Okonjo and T. A. Adeoye (Miss) for their encouragement and assistance.

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